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Application of novel unsaturated organosilane ethers in cationic UV-crosslinkable acrylic PSA systems

RAPID COMMUNICATION

Summary — This paper describes application possibilities of applying novel unsaturated — allyl and 1-propenyl butane-1,4-diol derivatives containing a trimethylsilane group [TMSAIE and DMSAIE, respectively, Formulas (I) and (III)] or a dimethylsilane group (TMSPnE and DMSPnE, respectively, Formulas (II) and (IV)] as cationic-crosslinking, reactive in result of UV radiation activity monomers in polyacrylate systems containing oxirane groups. Terpolymerization of 2-ethylhexyl acrylate with acrylic acid and glycidyl acrylate or metacrylate (GA and GMA, respectively) led to formation of pressure-sensitive adhesives (PSAs). Compositions containing such polyacrylates, unsaturated organosilane ethers (OE) and a Irgacure 261 as a were crosslinked at ambient temperature using a UV lamp. Adhesion to glass and cohesion of unmodified self-adhesives, as well as effect of OE on those properties were investigated. The best cohesion and adhesion levels for PSAs were achieved at approx. 3 wt. % of propenyl ethers (TMSPnE and DMSPnE). Those ethers also exhibited better crosslinking properties than TMSAIE and DMSAIE.

Key words: pressure-sensitive adhesives, cationic initiated UV-crosslinking, modification, unsaturated organosilane ethers, adhesion to glass, cohesion.

The UV initiated crosslinking of pressure-sensitive adhesives (PSAs) is one of the most rapidly developing fields in the entire coating and self-adhesives industry [1]. The low toxicity, cheapness, speed, control and ease of formulation, as well as usage are some of the main advantages of this growing UV-technology. UV light radiation is generally used to induce photochemical crosslinking of photoreactive formulations containing a certain type of unsaturated groups and appropriate photoinitiators. In recent years, there have been many developments in the synthesis and photochemical studies of photoinitiators, monomers, prepolymers and PSA polymers structures with more desirable properties, such as high reactivity in the photocrosslinking process, high quality of obtained polymer films, non-toxicity, cheapness and more easy handling [2—4].

Acrylates are known to be among the most reactive monomers polymerizing by a free radical mechanism. This feature, together with the remarkable chemical, optical and mechanical properties of the polymer obtained,

account for the great commercial success of UV-crosslinkable acrylic PSAs. The principal final properties of UV-crosslinked acrylic polymers depend primarily on the chemical structure of the functionalised chain segment. The strong photoreactivity and the large choice of UV-functionalised polymer segments have afforded these acrylic systems a leading position in UV-crosslinking applications, for example as self-adhesive products. The term “pressure-sensitive” is commonly used to designate a distinct category of self-adhesives that are aggressively and permanently tacky at room temperature and firmly adhere to a variety of dissimilar surfaces upon contact, with no more than finger or hand pressure [5].

The use of UV radiation to crosslinking acrylic PSAs is one of the alternative crosslinking methods to conventional crosslinking and also requires a photoinitiator or photosensitizer to absorb the impinging light and induce photocrosslinking.

With UV-crosslinked acrylic PSA, the ratio of tack and peel adhesion to shear strength (cohesion) can be varied within wide limits, by controlling the amounts of radiant energy applied to the adhesive film after it has been coated. Films formed by UV-crosslinked acrylic adhesive become more cohesive as more radiant energy is

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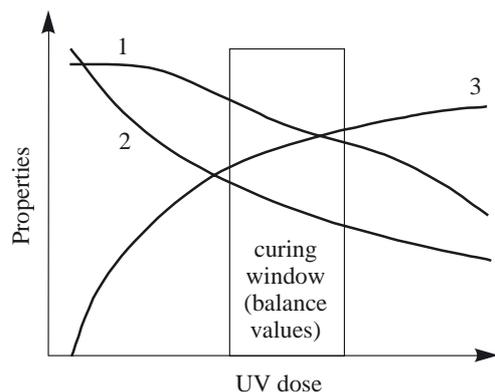


Fig. 1. Tack adhesion (curve 1), peel adhesion (curve 2) and shear strength (curve 3) as a function of UV dose

applied, while their tack and peel adhesion decreases. This effect is a consequence of the crosslinking that takes place when the film is exposed to UV light. The effect of the UV radiation dose (mJ/cm^2) on the adhesive properties and cohesion is shown schematically in Fig. 1. Whereas, a low UV-cured PSA coating exhibits good adhesion and medium cohesion, a well-cured PSA shows good cohesion and medium adhesion.

The allyl ether or the 1-propenyl ether of functionalized siloxanes are particularly interesting for the use in UV-crosslinking applications because of the unusual properties that they combine: thermal, chemical or physical properties of siloxanes (*e.g.* stability in a wide range of temperatures, good resistance to chemical agents, very low surface tension) and allyl ethers (primarily auto-oxidizing capacity) or 1-propenyl ethers (*e.g.* very high reactivity) [6–12].

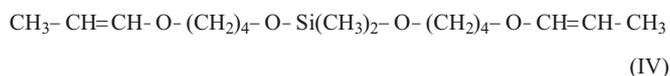
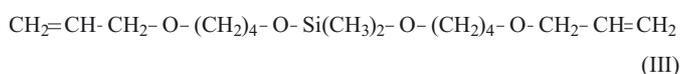
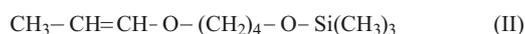
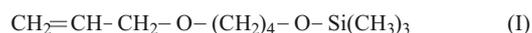
In this communication, new cationic UV-crosslinked acrylic PSA systems including modeling allyl-silane or 1-propenyl-silane ethers as crosslinkers are described.

EXPERIMENTAL

Materials

— 2-Ethylhexyl acrylate (2-EHA) and acrylic acid (AA) both from BASF (Germany);

— glycidyl acrylate (GA) and glycidyl methacrylate (GMA) from Nitto (Japan);



— 2,2'-azo-diisobutyronitrile (AIBN) from DuPont (USA);

— Irgacure 261 — cationic photoinitiator by Ciba (Germany);

— ethyl acetate from Shell (Netherlands) were used.

The unsaturated allylsilane silane ethers [TMSAIE, Formula (I) and TMSPnE, Formula (II)] or 1-propenyl-silane ethers [DMSAIE, Formula (III) and DMSPnE, Formula (IV)] were prepared by the authors.

Synthesis of ethyl acetate-borne acrylic PSAs

The solvent-borne acrylic PSAs were synthesized based on 2-EHA (60–85 wt. %), GA (10–35 wt. %) or GMA (10–35 wt. %) and AA at the solvent (ethyl acetate) boiling temperature in presence of 0.1 wt. % AIBN. Polymerization process lasted 5 hours at 50 wt. % solid content of acrylic polymer.

Modification, coating and UV-crosslinking of synthesized acrylic PSAs

The synthesized acrylic PSAs containing pendant oxirane groups into polymer chain were mixed with 1.0 wt. % Irgacure 261, modified using unsaturated organosilane ethers in concentrations between 1.0 to 5.0 wt. % (of acrylate content), cast with knife coater at about $60 \text{ g}/\text{m}^2$ on $36 \mu\text{m}$ polyester film Hostaphan RN from Hoechst (Germany), dried for 10 min at 105°C and cured 3 min with a UV lamp U 350-M-I-DL from IST Company with a UV-A wavelength between 315 to 380 nm at constant UV dose $300 \text{ mJ}/\text{cm}^2$. The UV-radiation can be measured using an integrating radiometer UVI-MAPTM UM 365 L-S manufactured by Electronic Instrumentation & Technology, Inc. (USA).

Methods

Adhesion on glass

The adhesion on glass is defined for the purpose of this paper as the force required to remove a coated flexible pressure-sensitive adhesive sheet material from a test panel measured at a 180° peel and rate of removal equal to AFERA 4001 (Association des Fabricants Europeens de Rubans Auto-Adhesifs). A sample of PSA-coated material 2.5 cm wide and 12.7 cm long is bonded to a horizontal target substrate surface of a clean glass test plate ensuring that at least 12.7 cm long. A 2 kg hard rubber roller is used to apply the strip. The free end of the coated strip is bended so that the angle of removal will be 180° . The steel test plate is clamped in the jaws of a tensile testing machine Zwick 1445, which is capable of moving at a constant rate of 300 mm per minute. The scale reading in Newtons is recorded as the tape is peeled off the steel surface as an arithmetic average from the results obtained for three evaluated samples.

Cohesion on glass

The cohesion on glass is defined for the purpose of this paper as measure of the shear strength or internal strength of a self-adhesive and represents. The amount of force required to pull an adhesive strip off a standard flat surface in a direction parallel to the surface to which it has been affixed with a definite pressure, according to AFERA 4012 at 20 °C and 70 °C. It is measured in Newtons for 4 h load times. Each test is conducted on two adhesive-coated strips applied to a standard stainless steel panel in a manner such that a 2.5×2.5 cm portion of the strip is in fixed contact with the panel with one end of the strip being free.

Other properties

The viscosity of the investigated adhesives was determined with a Rheomat RM 189 from Rheometric Scientific, with spindle No. 3 at 23 °C.

T_g value was measured with DSC 7 from Perkin-Elmer.

RESULTS AND DISCUSSIONS

Viscosity of acrylic PSAs

The typical properties of the solvent-borne acrylic PSAs, such as viscosity, have been tested in order to study the influence of the oxirane-monomers — GA and GMA (Table 1).

Table 1. Viscosity of acrylic PSAs containing GA or GMA

Amount of oxirane-monomer, wt. %	Viscosity, Pa · s	
	GA	GMA
10	1.25	0.86
15	1.84	1.10
20	2.67	1.48
25	4.10	2.30
30	6.30	3.15
35	8.95	4.03

Viscosity measurement reveals that the incorporation of the glycidyl acrylate or glycidyl methacrylate units into the polymer chain increases viscosity of the synthesized acrylic PSAs. A more pronounced growth of solution viscosity was observed in the case of GA.

Adhesion and cohesion of acrylic non-modified PSAs

The influence of the incorporated into polymer backbone oxirane-monomers (range from 10 to 35 wt. %) on, peel adhesion and shear strength of solvent-borne acrylic PSAs, is presented in Figs. 2 and 3.

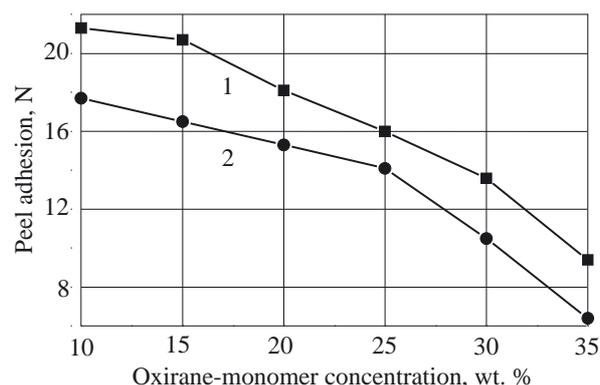


Fig. 2. Peel adhesion of UV-crosslinked acrylic PSAs as a function of oxirane-monomer concentration: 1 — GA, 2 — GMA

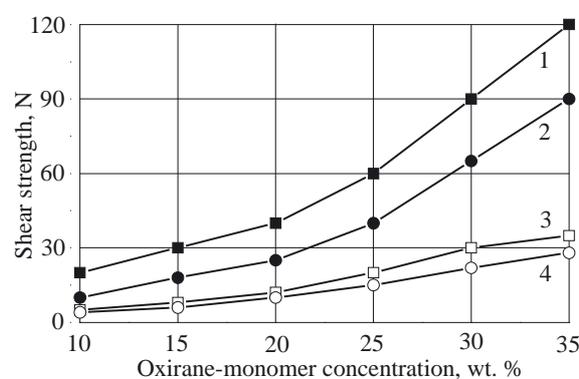


Fig. 3. Shear strength of UV-crosslinked acrylic PSAs as a function of oxirane-monomer concentration and temperature; 1 — GA (20 °C), 2 — GMA (20 °C), 3 — GA (70 °C), 4 — GMA (70 °C)

A more significant decrease in adhesion was noted using glycidyl methacrylate. A similar tendency was observed in the case of glycidyl acrylate. An increase of GA and GMA content decreases peel adhesion of the same UV-crosslinked acrylic PSAs. This effect is more noticeable in the case of GMA and correlates with the changes of glass transition temperature (T_g) of polymers synthesized with oxirane-monomers incorporated in the polymeric chain. The higher the T_g of polymer (T_g of GMA = +37 °C; T_g of GA = -26 °C), the lower the peel adhesion of the synthesized pressure-sensitive adhesives.

The higher cohesion (shear strength) of acrylic PSAs containing GA in both investigated temperatures is caused by the greater reactivity of acrylates in comparison to methacrylates.

The effect of modification on adhesion and cohesion of PSAs

The selected acrylic PSA containing 25 wt. % GA was used for further trials with different content of examined ethers. The crosslinking effect unsaturated of organosilane ethers [Formula (I)—(IV)] used as internal cross-

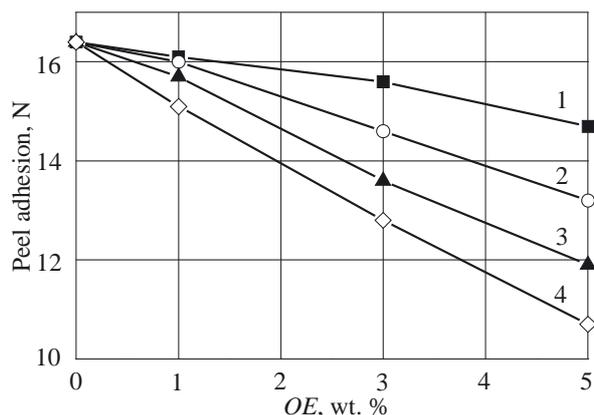


Fig. 4. Influence of the organosilane ether (OE) content on acrylic PSAs peel adhesion after UV-crosslinking; 1 — TMSPnE, 2 — DMSPnE, 3 — TMSAIE, 4 — DMSAIE

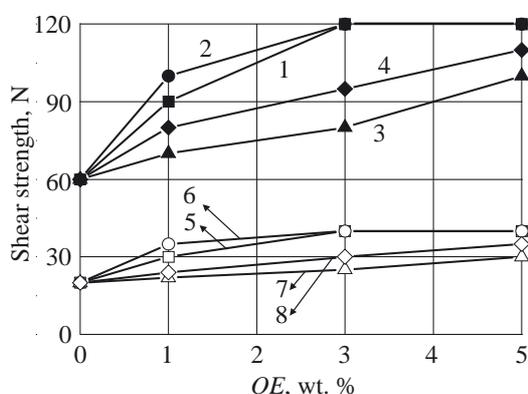


Fig. 5. Influence of the organosilane ether (OE) and temperature content on acrylic PSAs shear strength after UV-crosslinking; 1 — TMSPnE (20 °C), 2 — DMSPnE (20 °C), 3 — TMSAIE (20 °C), 4 — DMSAIE (20 °C), 5 — TMSPnE (70 °C), 6 — DMSPnE (70 °C), 7 — TMSAIE (70 °C), 8 — DMSAIE (70 °C)

linking agents after UV-exposure on peel adhesion and shear strength is illustrated in Figs. 4 and 5.

These results allow to conclude that a small decrease of UV-crosslinked acrylic PSA peel adhesion (Fig. 4) could be achieved by the use of the difunctional TMSPnE (curve 1) and the tetrafunctional DMSPnE (curve 2).

Addition of 1-propenyl organosilane ethers TMSPnE and DMSPnE strongly influences the shear strength properties of the UV-crosslinked acrylic PSAs (Fig. 5).

An increase in the content of those compounds (3—5 wt. %) produces, after UV exposure, a higher network density, leading to higher cohesion, measured at 20 °C and 70 °C in comparison with allyl organosilane ethers TMSAIE and DMSAIE. The best balance between peel adhesion and shear strength was achieved for approx. 3 wt. % of 1-propenyl organosilane ethers.

CONCLUSIONS

The investigations showed that monomers such as propenyl organosilane ethers possess the requisite reactivity facilitating their application in such high crosslinking speed applications as coatings and producing of cationic UV-crosslinkable acrylic PSAs for paper and plastic surfaces. In the tested solvent-borne acrylic pressure-sensitive adhesives, the photoreactivity of the evaluated 1-propenyl organosilane ethers TMSPnE and DMSPnE was superior to allyl organosilane ethers TMSAIE and DMSAIE. This type of developed acrylic PSAs can be used for bonding purposes in a wide variety of materials including glass and ceramics.

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